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# THE DECOMPOSITION OF METHANE ON REDUCED NICKEL.

By Masao Kubokawa.

It is well known that nickel is an excellent catalyst for the decomposition of methane,[1] and yet few studies on the reaction kinetics have been made. The present author had already investigated the decomposition of methane employing platinum wire as the catalyst, and demonstrated kinetically the retardation by carbon which was one of the reaction products and also the inhomogeneity of the catalytic surface.[2—4] In the present research, the author carried out a number of experiments below 500°C. with reduced nickel, and attempted to examine whether the same conclusion as in the case with platinum was obtained or not.

## Experimental Details.

**Apparatus.** The main part of the apparatus used is shown in Fig. 1. The reaction velocity was measured by the pressure change in the closed system. The pressure was read by means of a spring manometer S made of Pyrex glass, the image of its pointer being optically projected.[5]

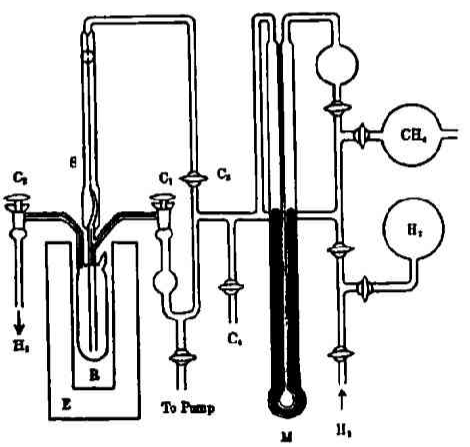


Fig. 1.—Apparatus.

S Spring manometer
R Reaction vessel
E Electric furnace
M Mercury manometer
C Stop cock

The reaction vessel R made of Pyrex glass held about 80 c.c. The wall of R was more than 2 mm. thick so that any diffusion of hydrogen or atmospheric gas might be negligible. The temperature of the electric furnace E was automatically regulated within ±0.5°C. during the course of the reaction.

The temperature regulator is shown in Fig. 2. The pointer of a millivoltmeter N connected with a thermo-elements was chopped by a nickel bar B every half a minute and when the temperature rose higher than desired, the switch M worked automatically to reduce

1) Egloff, "*The Reaction of Pure Hydrocarbons*" (A. C. S. monograph series), pp. 37-98 (1937).
2) Kubokawa, *Rev. Phys. Chem. Japan*, 11, 82 (1937).
3) Kubokawa, *ibid.*, 11, 96 (1937).
4) Kubokawa, *ibid.*, 11, 217 (1937).
5) Horiba, *ibid.*, 1, 269 (1927).

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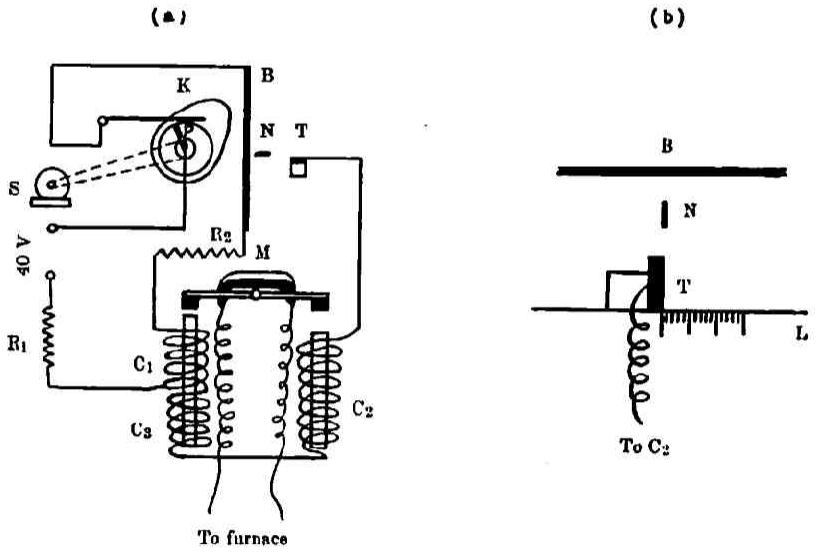


Fig. 2.—Temperature regulator of furnace.

| | |
|---|---|
| S Synchronous motor | T Temperature adjuster |
| K Cam | C Solenoid |
| P Platinum contact | M Mercury switch |
| N Pointer of millivoltmeter | R Resistance |
| B Chopper bar | L Scale of millivoltmeter |

the main current. Bakelite varnish was thinly applied on the pointer N not to let the current flow when it got in between B and the temperature adjuster T.[6] T is a piece of platinum plate attached to glass, and its right-hand side was adapted to the scale of a desired temperature as shown in Fig. 2 (b). Now, when N goes to the right-hand side of the edge of T and B chops N, the contact of P with K makes the current flow between B and T and then through all the solenoids of $C_1$, $C_2$ and $C_3$. The wires of $C_1$ and $C_3$ being wound reversely, the current is broken off by means of M by the action of $C_2$. The thermo-elements were coupled with chromel and alumel, and the calibration of the temperature reading was made with [Sn], [Cd], [Zn] and [Sb].

**Method.** In Fig. 1, a given amount of nickel oxide (usually 0.2 g.) was put in the reaction vessel R and hydrogen was passed over through $C_1$ at the speed of 1 litre per hour. After the reduction $C_2$ being closed, hydrogen was desorbed from $C_4$ by means of a mercury diffusion pump. Then, a given amount of methane was introduced to R from $C_1$. $C_1$ was shut quickly as soon as the gas reached thermal equilibrium in R. The initial pressures of methane in R were calculated by the preliminary experiments with air at various temperatures.

**Materials.** Nickel oxide used was prepared by calcination of nickel nitrate free from cobalt obtained by Kahlbaum at 350°C. The oxide was reduced with hydrogen for

6) Cf. Moriguchi, *Bull. Chem. Soc. Japan*, 54, 862 (1933).

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twelve hours at 500°C. Methane was prepared according to the reaction between aluminium carbide and water.[7] It was carefully purified and was proved to be absolutely pure by analysis.

## Experimental Results.

**Preliminary Experiments.**

The decomposition of methane is a reversible reaction, which is expressed by

$$CH_4 \rightleftarrows C\,(\text{graphite}) + 2H_2.$$

The equilibrium constant of this reaction must be taken into account in discussing the kinetics of the reaction. It, however, remarkably varies according to investigators, so in the present experiment the equilibrium constant was carefully determined. Employing 0.2 g. of nickel oxide, it was ascertained that equilibrium was established within 18 hours when the initial pressure of methane was below 5 cm. and the temperature was above 420°C.[7]

The equilibrium constant $K_p$ was calculated according to

$$K_p = \frac{(P_{CH_4})_e}{(p_{H_2})_e^2} = \frac{2p_0 - p_e}{4(p_e - p_0)^2} \times 76,$$

where $p_0$ is the initial pressure of methane in cm., and $p_e$ the equilibrium pressure of a methane and hydrogen mixture in cm. In this calculation the adsorption of hydrogen was neglected, because it was ascertained to be very small.

The values thus calculated are tabulated in Table 1.

Table 1.

| Tem. °C | $p_0$ (cm.) | $p_e$ (cm.) | % decomp. | $K_p$ |
|---|---|---|---|---|
| 450 | 3.32 | 5.42 | 63.3 | 5.27 |
| 460 | 1.33 | 2.30 | 77.4 | 4.50 |
| 482 | 2.54 | 4.34 | 70.9 | 3.75 |

The values of $K_p$ are in agreement with those of Gordon and Barnes[8] ($K_p$= 11.0 at 427°C.; 1.68 at 527°C.) calculated from the absolute entropy. It cannot be considered that methane is completely decomposed unless the initial pressure is far lower than in the above table. Therefore, only the initial stage of the reaction can be discussed kinetically without taking a reverse reaction into consideration.

7) Equilibrium was ascertained by no change of the pressure during 18—45 hours from the start.

8) *J. Phys. Chem.*, 36, 2601 (1932).

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The following experiment was carried out to see if the reaction proceeded only on the surface of nickel or not. Methane at a pressure of 3.6 cm. was put in an empty vessel at 500°C. for one hour. In practice, no variation in pressure was observed, which indicates that both the catalytic action of the glass walls and the reaction in the gaseous phase can be neglected.

It has been admitted that the catalytic action of carbon formed which is considered to be graphite[9] is far less than that of nickel, and even in the case of the greatest amount of carbon in the present research the amount is a tenth of that of the catalyst, so that the catalytic action of carbon need not be taken into account.

It has been also admitted that the formation of other gases than hydrogen is negligible in the presence of such a metallic catalyst as nickel.[1]

**The Reaction Velocity with Activated Nickel.**

The decrease in activity of a nickel catalyst in repeated use was similar to the case with a platinum catalyst.[2]

Under the following experimental conditions activity could be kept constant by passing hydrogen for twelve hours at 500°C. every time the experiment was carried out. Thus the catalyst may be regarded as activated by this treatment. The recovery of activity with hydrogen may be interpreted thus: nickel is recovered from the carbide in the centres of higher activity according to the reaction,[10]

$$Ni_xC + 2H_2 \rightarrow xNi + CH_4.$$

The experimental results obtained at 500°C. employing the nickel thus activated with hydrogen are given in Tables 2—5.

In these tables, $x$ is the decomposed amount of methane at time $t$(min.), which is denoted by pressure in cm.; $k_m$ is $\frac{1}{t}\log_e\frac{a}{a-x}$, where $a$ is the initial amount of methane denoted by the initial pressure $p_0$(cm.); $k$ and $n$ are constants

9) Kusama and Uno, *Bull. Inst. Phys. Chem. Research*, 8, 1 (1929).

10) The presence of nickel carbide, $Ni_3C$, has been ascertained under a certain condition [Bahr, *Ber. Dtsch. chem. Ges.*, 61, 2177 (1928); Tsuchiya, *Bull. Phys. Chem. Research*, 10, 556, 951 (1931).], and it has been reported that nickel carbide becomes unstable at higher temperatures than 420°C. [Scheffer, Dokkum and Al, *Rec. trav.*, 45, 803 (1926); Schmidt, *Z. anorg. Chem.*, 216, 85 (1933).]. Therefore, in the present experiment carried out above 460°C. the formation of carbide or adsorption compound is considered to take place only on the active patches of the surface. This consideration is justified by the following facts: (1) The equilibrium constant was in good agreement with that obtained theoretically. If equilibrium is established between methane, hydrogen and carbide (not carbon), the equilibrium constant will not agree. (2) The activity of the catalyst decreased in repeated experiments, but ceased to decrease in a certain degree (see the next paragraph). (3) The activity was easily recovered with hydrogen.

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in the following equation:

$$\frac{dx}{dt}=k\frac{(a-x)}{x^n}. \qquad (1)$$

$k$ and $n$ were obtained from the integrated form:

$$k_m=\frac{n}{a}\cdot\frac{x}{t}+\frac{k}{a^n}. \qquad (1)'$$

$n$ was found from the slope of the straight line obtained by plotting $k_m$ and $x/t$, and, it being substituted in the equation, $k$ was calculated. The relation between $x$ and $t$ and that between $k_m$ and $x/t$ are shown in Figs. 3 and 4 respectively.

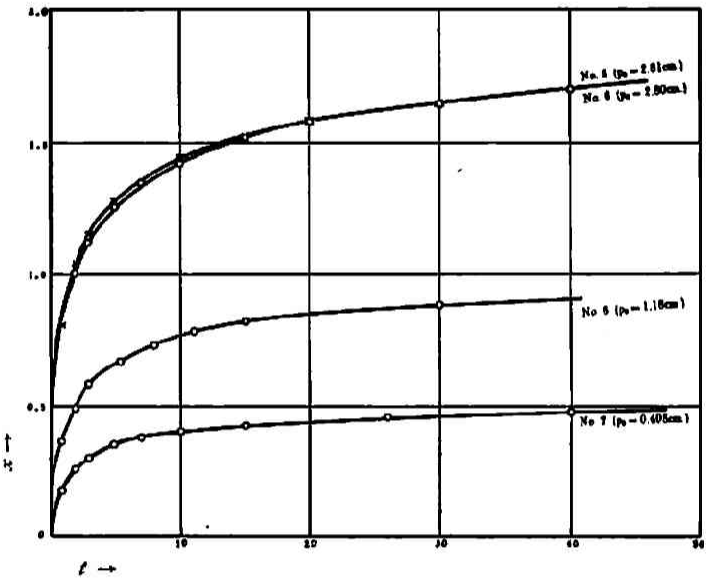


Fig. 3.—Expts. at 500°C. with activated Ni.

Table 2.

Expt. 5. (500°C.)
$p_0$=2.81cm. $n$=1.26

| $t$ (min). | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k$ |
|---|---|---|---|---|---|
| 1 | 3.610 | 0.800 | 0.1455 | 0.800 | — |
| 2 | 3.851 | 1.041 | 0.1005 | 0.521 | — |
| 3 | 3.961 | 1.151 | 0.0763 | 0.384 | 0.013 |
| 5 | 4.098 | 1.288 | 0.0533 | 0.258 | 0.026 |
| 8 | 4.238 | 1.428 | 0.0385 | 0.179 | 0.031 |
| 10 | 4.251 | 1.441 | 0.0312 | 0.144 | 0.027 |
| 15 | 4.320 | 1.510 | 0.0233 | 0.107 | 0.013 |
| 20 | 4.382 | 1.572 | 0.0178 | 0.0786 | 0.021 |
| 30 | 4.468 | 1.658 | 0.0129 | 0.0552 | 0.008 |
| | | | | | mean 0.020 |

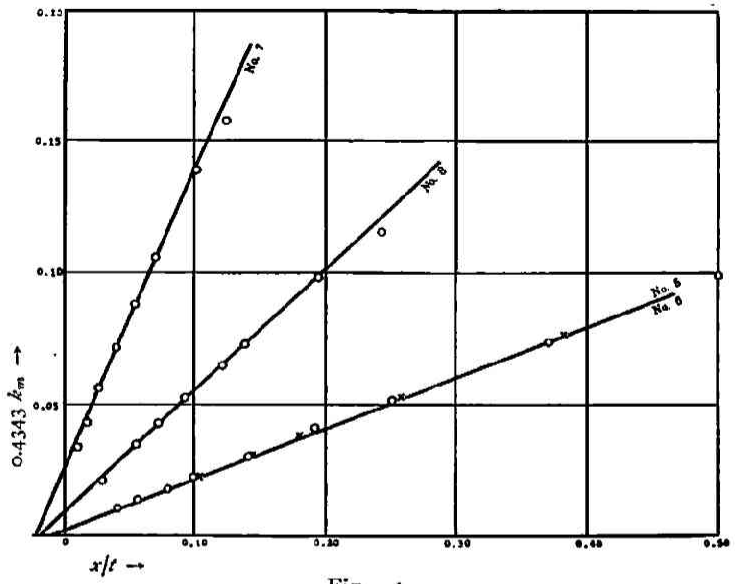


Fig. 4.

Table 3.

Expt. 6. (500°C.)

$p_0$=2.80cm. $n$=1.26

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k$ |
|---|---|---|---|---|---|
| 1 | 3.523 | 0.723 | 0.130 | 0.723 | — |
| 2 | 3.799 | 0.999 | 0.0959 | 0.500 | — |
| 3 | 3.912 | 1.112 | 0.0733 | 0.371 | — |
| 5 | 4.050 | 1.250 | 0.0513 | 0.250 | 0.021 |
| 7 | 4.145 | 1.345 | 0.0410 | 0.192 | 0.029 |
| 10 | 4.220 | 1.420 | 0.0307 | 0.142 | 0.025 |
| 15 | 4.320 | 1.520 | 0.0227 | 0.101 | 0.024 |
| 20 | 4.371 | 1.571 | 0.0179 | 0.0785 | 0.022 |
| 30 | 4.441 | 1.641 | 0.0128 | 0.0547 | 0.018 |
| 40 | 4.500 | 1.700 | 0.0101 | 0.0425 | 0.015 |
| | | | | | mean 0.022 |

Table 4.

Expt. 7. (500°C.)

$p_0$=0.498cm. $n$=1.28

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k$ |
|---|---|---|---|---|---|
| 1 | 0.674 | 0.176 | 0.189 | 0.176 | — |
| 2 | 0.755 | 0.257 | 0.158 | 0.128 | 0.016 |
| 3 | 0.804 | 0.306 | 0.138 | 0.102 | 0.033 |
| 5 | 0.848 | 0.350 | 0.105 | 0.070 | 0.026 |
| 7 | 0.876 | 0.378 | 0.0883 | 0.054 | 0.027 |
| 10 | 0.898 | 0.400 | 0.0706 | 0.049 | 0.025 |
| 15 | 0.923 | 0.425 | 0.0556 | 0.028 | 0.023 |
| 25 | 0.953 | 0.455 | 0.0426 | 0.018 | 0.021 |
| 40 | 0.974 | 0.476 | 0.0336 | 0.012 | 0.019 |
| | | | | | mean 0.024 |

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Table 5.

Exp. 8. (500°C.)

$p_0$=1.18cm. $n$=1.26

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k$ |
|---|---|---|---|---|---|
| 1 | 1.534 | 0.354 | 0.155 | 0.357 | — |
| 2 | 1.663 | 0.483 | 0.115 | 0.242 | — |
| 3 | 1.758 | 0.578 | 0.0977 | 0.193 | 0.023 |
| 5.5 | 1.842 | 0.662 | 0.0651 | 0.120 | 0.027 |
| 8 | 1.907 | 0.727 | 0.0520 | 0.0908 | 0.028 |
| 11 | 1.956 | 0.776 | 0.0423 | 0.0705 | 0.027 |
| 15 | 1.989 | 0.809 | 0.0335 | 0.0539 | 0.024 |
| 30 | 2.060 | 0.880 | 0.0198 | 0.0293 | 0.018 |
| | | | | | mean 0.0245 |

As seen in Tables 2—5, $k$ is fairly constant, which justfies not only the applicability of the above-mentioned equation but also the reproducibility of the experiments. In each experiment, the data obtained within three minutes from the start have been omitted because the error in the initial pressure $p_0$ affected much. $n$ is a constant named "retardation exponent,"[3] and is much larger than 1 when a fresh catalyst is used as in the present experiment.

**Experiments at Lower Temperatures.**

As one of the results obtained below 500°C., that obtained at 460°C. is given in Tables 6 and 7. The relation between $x$ and $t$ and the linear relation between $k_m$ and $x/t$ are shown in Figs. 5 and 6 respectively.

Table 6.

Expt. 9. (460°C.)

$p_0$=2.78cm. $n$=1.08

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k$ |
|---|---|---|---|---|---|
| 1 | 3.110 | 0.330 | 0.0548 | 0.330 | — |
| 2 | 3.227 | 0.447 | 0.0382 | 0.224 | — |
| 5 | 3.423 | 0.643 | 0.0228 | 0.129 | 0.007 |
| 7 | 3.553 | 0.773 | 0.0202 | 0.110 | 0.011 |
| 10 | 3.680 | 0.900 | 0.0170 | 0.0900 | 0.012 |
| 15 | 3.831 | 1.051 | 0.0137 | 0.0707 | 0.012 |
| 20 | 3.896 | 1.116 | 0.0111 | 0.0558 | 0.012 |
| 25 | 3.928 | 1.148 | 0.00925 | 0.0459 | 0.010 |
| 30 | 3.945 | 1.165 | 0.00786 | 0.0388 | 0.009 |
| | | | | | mean 0.0104 |

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Table 7.

Expt. 10. (460°C.)

$p_0$=1.535cm. $n$=1.00

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k$ |
|---|---|---|---|---|---|
| 2 | 1.760 | 0.225 | 0.0344 | 0.113 | 0.009 |
| 3 | 1.809 | 0.274 | 0.0285 | 0.0913 | 0.009 |
| 6 | 1.940 | 0.405 | 0.0222 | 0.0675 | 0.012 |
| 8 | 2.021 | 0.486 | 0.0207 | 0.0628 | 0.012 |
| 13 | 2.119 | 0.584 | 0.0160 | 0.0450 | 0.012 |
| 20 | 2.233 | 0.693 | 0.0132 | 0.0349 | 0.012 |
| 30 | 2.335 | 0.800 | 0.0109 | 0.0267 | 0.012 |
| 40 | 2.415 | 0.880 | 0.00925 | 0.0220 | 0.011 |
| | | | | | mean 0.0111 |

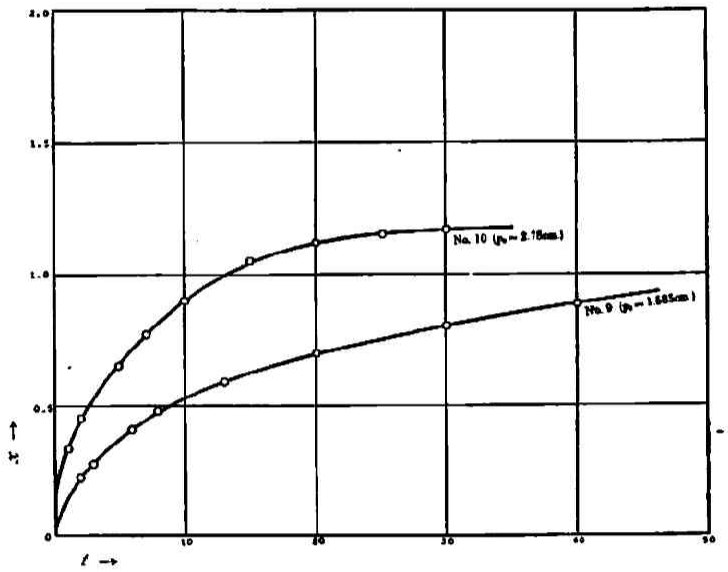


Fig. 5.—Expts. at 460°C. with activated Ni.

Comparing this with that obtained at 500°C., it is seen that the retardation exponent $n$ decreases as the velocity constant $k$ does.

Assuming that the reaction velocity obeys Arrhenius' equation, the heat of activation in the temperature range between 460° and 500°C. was calculated and the value of 20.000 cal./g. mol was obtained.

**The Reaction Velocity with Unactivated Nickel.**

When the catalyst is only evacuated without passing hydrogen after an experiment, in the next run its activity becomes a little lower. This decrease in activity, however, gradually ceases and the activity seems to approach a certain

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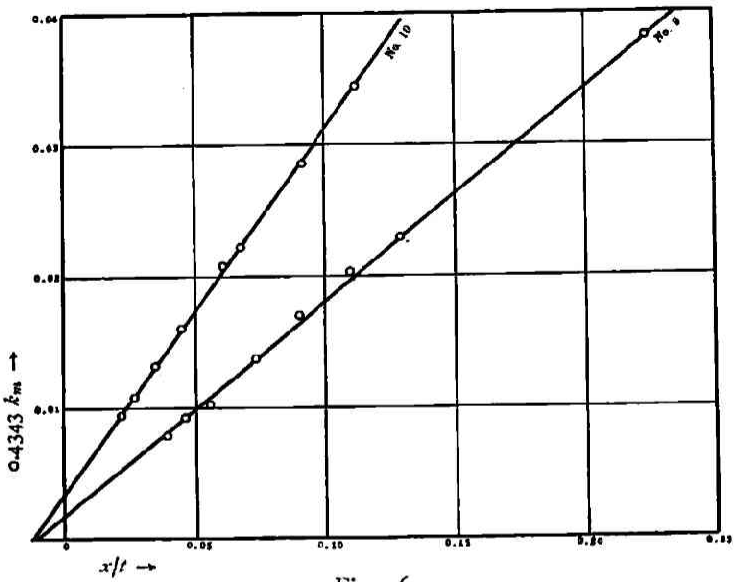


Fig. 6.

value in repeated experiments. As for a catalyst which is considerably active at 500°C., decrease in its activity by repeated use is shown in Fig. 7. The curves in Fig. 7 slope gently without rising steeply at the beginning, being quite different from that in Fig. 3. The relation between $k_m$ and $x/t$, however, is linear as seen in Fig. 8. In Fig. 8, the retardation exponent obtained gradually becomes small during repeated experiments (see Tables 8—13). As the retardation ex-

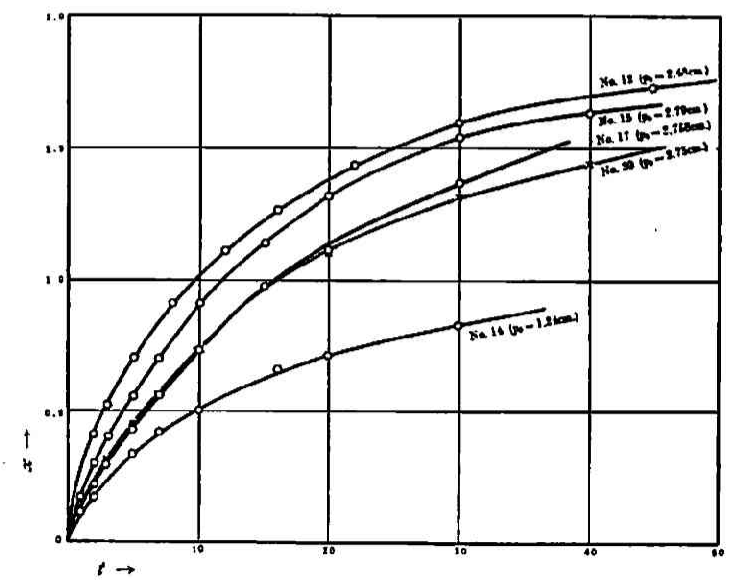


Fig. 7.—Expts. at 500°C. with unactivated Ni.

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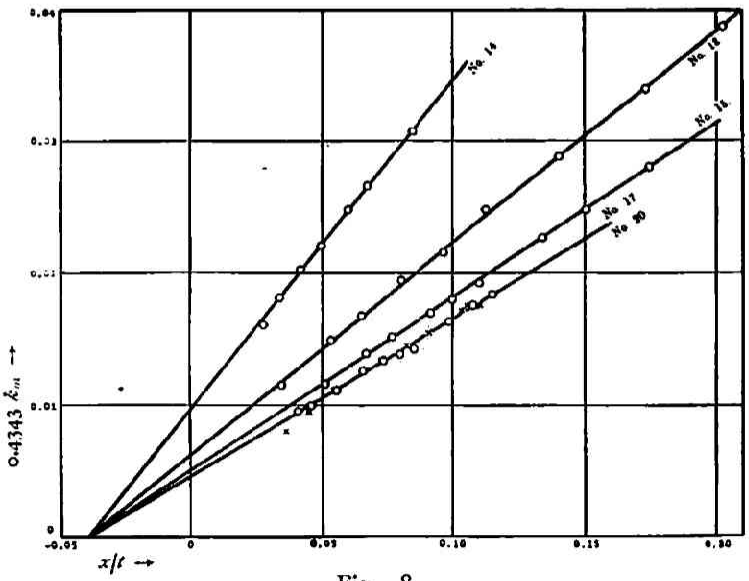


Fig. 8.

ponents are always smaller than 1, the reaction velocity should be more exactly expressed by the Langmuir-Hinshelwood theory

$$\frac{dx}{dt}=\frac{k'(a-x)}{1+bx}, \qquad (2)$$

where $b$ is the adsorption coefficient of the reaction product.

Integrating the equation, we have

$$k_m=\left(\frac{b}{1+ab}\right)\frac{x}{t}+\frac{k'}{1+ab}. \qquad (2)'$$

After $b$ was obtained from Fig. 8, $k'$ was calculated from this equation, which is given in Tables 8—12. $b$ and $k'$ diminish every time the experiment

Table 8.

Expt. 12. (500°C.)
$p_0$=2.48cm. $b$=4.00 ($n$=0.91)

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k'$ |
|---|---|---|---|---|---|
| 2 | 2.885 | 0.405 | 0.0388 | 0.203 | 0.163 |
| 3 | 2.999 | 0.519 | 0.0340 | 0.173 | 0.163 |
| 5 | 3.180 | 0.700 | 0.0288 | 0.140 | 0.164 |
| 8 | 3.390 | 0.910 | 0.0248 | 0.114 | 0.167 |
| 12 | 3.586 | 1.106 | 0.0214 | 0.0922 | 0.169 |
| 16 | 3.749 | 1.269 | 0.0195 | 0.0793 | 0.173 |
| 22 | 3.900 | 1.420 | 0.0168 | 0.0645 | 0.164 |
| 30 | 4.005 | 1.595 | 0.0147 | 0.0532 | 0.161 |
| 45 | 4.205 | 1.725 | 0.0115 | 0.0383 | 0.136 |
| | | | | | mean 0.162 |

Table 9.

Expt. 14. (500°C.)

$p_0$=1.24cm+1.525cm ($H_2$) $b$=2.00 ($n$=0.70)

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k'$ |
|---|---|---|---|---|---|
| 2 | 2.934 | 0.169 | 0.0308 | 0.0845 | 0.078 |
| 5 | 3.097 | 0.332 | 0.0266 | 0.0664 | 0.080 |
| 7 | 3.179 | 0.414 | 0.0248 | 0.0591 | 0.081 |
| 10 | 3.260 | 0.495 | 0.0221 | 0.0495 | 0.078 |
| 16 | 3.423 | 0.658 | 0.0203 | 0.0411 | 0.082 |
| 20 | 3.472 | 0.707 | 0.0181 | 0.0336 | 0.078 |
| 30 | 3.595 | 0.830 | 0.0160 | 0.0277 | 0.073 |
| | | | | | mean 0.079 |

Table 10.

Expt. 15. (500°C.)

$p_0$=2.79cm. $b$=1.79 ($n$=0.84)

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k'$ |
|---|---|---|---|---|---|
| 1 | 2.964 | 0.174 | 0.0280 | 0.174 | 0.075 |
| 2 | 3.090 | 0.300 | 0.0247 | 0.150 | 0.082 |
| 3 | 3.191 | 0.401 | 0.0227 | 0.134 | 0.074 |
| 5 | 3.342 | 0.552 | 0.0191 | 0.110 | 0.067 |
| 7 | 3.480 | 0.698 | 0.0179 | 0.0997 | 0.073 |
| 10 | 3.700 | 0.910 | 0.0171 | 0.0910 | 0.073 |
| 15 | 3.928 | 1.138 | 0.0152 | 0.0759 | 0.074 |
| 20 | 4.108 | 1.318 | 0.0139 | 0.0659 | 0.073 |
| 30 | 4.330 | 1.540 | 0.0116 | 0.0513 | 0.068 |
| 40 | 4.420 | 1.630 | 0.0095 | 0.0408 | 0.058 |
| | | | | | mean 0.072 |

Table 11.

Expt. 17. (500°C.)

$p_0$=2.758cm. $b$=1.34 ($n$=0.78)

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k'$ |
|---|---|---|---|---|---|
| 1 | 2.873 | 0.115 | 0.0185 | 0.115 | 0.046 |
| 2 | 2.974 | 0.216 | 0.0177 | 0.108 | 0.047 |
| 3 | 3.053 | 0.296 | 0.0164 | 0.0983 | 0.046 |
| 5 | 3.170 | 0.422 | 0.0141 | 0.0844 | 0.039 |
| 7 | 3.313 | 0.555 | 0.0139 | 0.0793 | 0.044 |
| 10 | 3.488 | 0.730 | 0.0134 | 0.0730 | 0.047 |
| 15 | 3.733 | 0.975 | 0.0126 | 0.0650 | 0.049 |
| 20 | 3.863 | 1.105 | 0.0111 | 0.0553 | 0.046 |
| 30 | 4.128 | 1.370 | 0.0099 | 0.0457 | 0.036 |
| | | | | | mean 0.044 |

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Table 12.
Expt. 20. (500°C.)
$p_0$=2.750cm. $b$=1.32 ($n$=0.78)

| $t$ (min.) | $p$ (cm.) | $x$ (cm.) | 0.4343 $k_m$ | $x/t$ | $k'$ |
|---|---|---|---|---|---|
| 1 | 2.860 | 0.110 | 0.0177 | 0.110 | 0.043 |
| 2 | 2.960 | 0.210 | 0.0177 | 0.105 | 0.050 |
| 3 | 3.060 | 0.310 | 0.0173 | 0.103 | 0.048 |
| 5 | 3.203 | 0.453 | 0.0156 | 0.0906 | 0.046 |
| 7 | 3.322 | 0.572 | 0.0144 | 0.0817 | 0.045 |
| 10 | 3.480 | 0.730 | 0.0134 | 0.0730 | 0.046 |
| 20 | 3.851 | 1.101 | 0.6111 | 0.0551 | 0.045 |
| 30 | 4.066 | 1.316 | 0.00943 | 0.0439 | 0.042 |
| 40 | 4.190 | 1.440 | 0.00805 | 0.0360 | 0.038 |
| | | | | | mean 0.045 |

was carried out, but they approach certain values as shown in Table 13. After Expt. 17 two experiments with a large amount of methane (50 cm. pressure) at 500°C. for 24 hours were carried out, but both the values of $b$ and $k'$ obtained remain constant as seen in Expt. 20.

Table 13.

| Expt. No. | $n$ | $b$ | $k'$ | $k'/b$ |
|---|---|---|---|---|
| 12 | 0.91 | 4.00 | 0.162 | 0.0405 |
| 14 | 0.70 | 2.00 | 0.079 | 0.0395 |
| 15 | 0.84 | 1.79 | 0.072 | 0.0402 |
| 17 | 0.78 | 1.34 | 0.044 | 0.0328 |
| 20 | 0.78 | 1.32 | 0.045 | 0.0341 |

**Effect of Added Hydrogen and the Cause of the Retardation.**

Preliminary addition of hydrogen does not affect the reaction velocity, and this is different from the case of the homogeneous decomposition of methane.[11] As an example, the result obtained with mixed hydrogen at a partial pressure a little higher than that of methane has been given in Table 9 (Expt. 14). It is considered from this experiment that the hydrogen formed during the decomposition of methane does not retard the reaction. As for the carbon crystals formed in the course of the reaction, they are assumed to have no effect on the reaction, for the activity of the catalyst becomes constant after it has decreased in a certain degree in spite of the accumlation of carbon crystals.[12] Therefore, the retarda-

11) e.g. Holliday and Exell, *J. Chem. Soc.*, 1929, 1066; 1931, 1594.

12) The same result has been obtained by other investigator: Yamaguchi, *J. Chem. Soc. Japan*, 48, 321 (1927); *Bull. Chem. Soc. Japan*, 2, 289 (1927).

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tion of the reaction velocity represented by $x$ in the denominator of equation (1) or (2) should be caused by the adsorption of carbon atoms or the decomposed fragments of methane molecules, such as $CH_3$, $CH_2$ and CH. The carbon atoms are considered to be adsorbed irreversibly when it is adsorbed on highly active patches of the nickel surface.

## Conclusion

It has been admitted that various active centres possessing different degrees of activities exist on a catalytic surface. Such inhomogeneity of the catalytic surface as this was, for the first time, kinetically demostrated by Horiba and Ri[13] from their experiments on the decomposition of carbon monoxide with nickel catalysts. The results of the present experiment lead to the same conclusion.

In the present experiment of measuring the decomposition velocity of methane on a nickel catalyst, the relation $n > 1$ always held in the velocity equation $dx/dt = k(a-x)/x^n$ in the case where an active catalyst was used, as in the case of a platinum catalyst. As already discussed in the case of platinum catalyst[3] it is difficult to explain this velocity equation by the assumption that the surface of the catalyst is homogeneous, but it is satisfactorily done by the assumption that the carbon atoms are adsorbed on the highly active centres forming nickel carbide or adsorption compound with nickel, while on the less active centres they are in two-dimentional adsorption equilibrium, being reversibly adsorbed.[14]

Though $n$ varies under various conditions, it presents a similar tendency to that in the case of platinum:

1) When the reaction temperature falls, $n$ decreases as $k$ does. This is explained thus: at lower temperatures the reactivity of such active centres as form the adsorption compound diminishes, so that the active centres will come to adsorb the carbon atoms reversibly. The values of $n$ obtained using an active nickel are tabulated in Table 14.

2) In repeated use of the catalyst without being reduced, $n$ becomes smaller than 1 and further diminishes. This is explained thus: the number of highly active centres are decreased by carbon adsorbing irreversibly every time the experiment is carried out and so the surface left alive from poisoning gradually becomes homogeneous in nature. Even to this case the applicability of the

13) Horiba and Ri, *Rev. Phys. Chem. Japan*, 4, 73 (1930); Ri, *ibid.*, 5, 41 (1931); Ri, *Rec. trav.*, 51, 641 (1931); Ri and Nagamitsu, *Rev. Phys. Chem. Japan*, 9, 140 (1935).

14) Schwab and Pietch, *Z. physik. Chem.* [B], 1, 385 (1929); *Z. Elektrochem.*, 35, 135 (1929).

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Table 14.

| Temp. °C. | Expt. No. | $n$ | $k$ |
|---|---|---|---|
| 500 | 5 | 1.26 | 0.020 |
| | 6 | 1.26 | 0.022 |
| | 7 | 1.28 | 0.024 |
| | 8 | 1.26 | 0.0245 |
| 460 | 9 | 1.08 | 0.0104 |
| | 10 | 1.00 | 0.0111 |

Langmuir-Hinshelwood theory is insufficient, for the adsorption coefficient $b$ of the carbon atoms, which has been obtained by the application of the theory, varies in each experiment. The results obtained at 500°C. are given in Table 13. During Expts. 12—17, $b$ and $k'$ gradually decrease. This fact shows that the irreversible adsorption is also taking place in the course of the reaction.

As to this table, it is interesting to mention that $k'/b$ is constant in spite of variations in $b$ and $k'$.

## Summary

1) The equilibrium constant and the reaction velocity of the catalytic decomposition of methane on reduced nickel have been measured in the temperature range between 420°—500°C. below the pressure of 30 mm. The reaction velocity in the initial stage is always expressed by

$$\frac{dx}{dt} = k\frac{(a-x)}{x^n},$$

where $a$ is the initial amount of methane, $x$ the decomposed amount at the time $t$, $k$ and $n$ constants.

2) The retardation exponent $n$ is always larger than 1 when the catalyst has been activated by reduction with hydrogen, and it becomes smaller than 1 when the catalyst is used repeatedly without being reduced and also when the temperature is lowered. The effect of added hydrogen has not been observed. These results are in agreement with those in the case of platinum calalyst.

3) That the retardation exponent is larger than 1 is considered to show kinetically the heterogeneity of the surface as in the case of platinum catalyst: such an irreversible reaction as the formation of nickel carbide takes place on the active patches, while in the less active patches two-dimentional adsorption equilibrium is established between reacting components, the strong adsorption of carbon atoms retarding the reaction.

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4) To the case where the retardation exponent is smaller than 1 the Langmuir-Hinshelwood equation has been applied, but it has been pointed out that in this case the irreversible adsorption of carbon atoms must be also taken into consideration.

5) For the catalytic decomposition of methane including irreversible reaction, 20 kcal./g. mol has been obtained as the apparent heat of activation.

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